Proceedings of the 4th International Conference on Environmental Pollution and Remediation
Prague, Czech Republic, August 11-13, 2014
Paper No. 71

Leaching and Mechanical Behaviour of Solidified/Stabilized Nickel Contaminated Soil with Cement and Geosta

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Abstract -In the present work, solidification/stabilization (S/S) of nickel contaminated soil using ordinary Portland cement (OPC) and Geosta® (specifically manufactured additive agent) was carried out. The effects of different binder combinations of OPC and Geosta wt% in the S/S mix designs and the physical and chemical characteristics of the treated samples were investigated. The mechanical characteristic studied was compressive strength while chemical characterization of the samples was focused on the leachability of nickel. Results indicated that the optimum mix design, in terms of mechanical efficiency, was 10% OPC wt% and 4.2 wt% Geosta while in terms of chemical efficiency 5% OPC wt% and 1.4 wt% Geosta.

Keywords: Cement, Nickel, Waste management, Mechanical properties, Leaching.

1. Introduction

Stabilization/solidification (S/S) is one of the major methods in treating hazardous wastes prior to land disposal and also an effective technique for reducing the leachability of contaminants in soils like, heavy metals (Gupta, 2007; Kogbara et al., 2011). The entrapment of wastes that express hazardous characteristics within a cementitious matrix (solidification) and the binding of the contaminants (organic or inorganic) of a hazardous stream into a stable insoluble form (stabilization) are the mechanisms that best describe the principle behind solidification and stabilization (S/S) treatment. Solidification and stabilization (S/S) related processes such as chemical and physical stabilization of contaminants, dangerous to natural and build environment, have been identified as Best Demonstrated Available Technology (BDAT) for 57 different hazardous wastes under the Resource Conservation and Recovery Act (RCRA) (Yin**,** 2007; Paria et al., 2006).

Heavy metals are well known to be toxic to most organisms and harmful to the environment when present in excessive concentrations (Giller,1998; Hsiau et al., 1998). Nickel has recently become a serious pollutant which is mainly released, from metal processing operations and from the increased combustion of coal and oil (Kabata-Pendias et al., 2007). Nickel is considered to be one of the most dangerous chemical elements, which may cause permanent soil contamination due to its specific physicochemical properties and mechanism of action (Janicka,2003; Aydinalp et al., 2003).

Portland cement is the most commonly used primary binder for S/S matrix because it can restrict the mobility of heavy metals due to high pH and due to its capability to precipitate the metals in insoluble forms(Gupta, 2007; Kogbara et al., 2011). Yin et al. 2007 studied S/S of nickel hydroxide sludge using ordinary Portland cement (OPC) and oil palm ash (OPA). The authors (Yin et al. 2007**)** investigated the possibility to reduce the availability of Ni by increasing the amount of OPA and reducing the amount of OPC and found that the optimum mix design is 15 wt% OPA, 35 wt% OPC and 50 wt% sludge. Grega et al., 2011 examined the effectiveness of ordinary Portland cement (OPC), calcium aluminate cement (CAC), pozzolanic cement (PC) and different additives in immobilizing Cd, Pb, Zn, Cu, Ni and As, in contaminated soil. The effectiveness was evaluated using leaching experiments, mechanical strength and geochemical modeling. Based on the model calculation, the most efficient S/S formulation was CAC + Akrimal (a cement repair mortar modified with aqueous acrylic polymer dispersion), which reduced soil leachability of Ni up to 4,7 times. Eisa et al., 2011 investigated the immobilization of Ni(II) in various cement matrices (neat Portland cement in absence and presence of water reducing- and water repelling-admixtures as well as blended cement with kaolin) using the S/S technique. The degree of immobilization was assessed by using static mode and semi static mode of leaching and it was found to be very high (99%).

Secondary binders could be described as materials that are not very effective on their own, when used in S/S methods, and are useful only when used in conjunction with lime or cement. Secondary additives are used mostly as stabilizers comprised of fly ash, zeolites, calcium or sodium or ammonium chlorides, enzymes, polymers, and potassium compounds . Several researches have shown that zeolites may be more suitable than other additives for the decontamination of soils polluted by heavy metals because they adjust soil pH value and as cation exchangers (Shi, 2009; Mahabadi et al., 2007). Shanableh et al., 1996, used a natural zeolite as additive to reduce the leaching of Pb^{2+}+, Cd^{2+} and Ni^{2+} from a contaminated soil and found that using up to 50% additive, nickel leaching was reduced by a maximum of approximately 50%. Belviso et al., 2010, in their study, used an artificially Ni contaminated soil ,treated with coal fly ash for synthesizing zeolite at low temperatures and they found that newly-formed zeolites reduce the toxicity of the element in the polluted soil.

The aim of this work was to use ordinary Portland cement (OPC) and Geosta at different binder combinations in order to study the strength development as well the leachability aspects of OPC - treated Ni contaminated soil.

2. Materials and Methods

The experiments were carried out using an artificially restored and polluted soil. . For the soil, the particle size distribution (ASTM D6913) and the British Standard light compaction test (BS 1377) were applied. After particle size analysis, the soil consisting of 60% of sand (ranging between fine, medium and coarse sand) and 40% of fine gravel. Therefore, the soil could be described as a well graded gravelly sand. Regarding the compaction test, the values of the optimum water content and the maximum dry density are 8,1% and 1724 kg/m^3, respectively. The nickel used was Nickel (II) sulfate hexahydrate ($NiSO_4.6H_2O$) which had a solubility of 625 g/l at 20°C and a final concentration of 2300 mg/kg by weight of soil. The experimental program consisted of one primary binder (Medium strength, type I 35/A Portland cement) at different quantities (5%, 7.5% and 10% by dry weight of the soil) and Geosta at 1.4% (100gr), 2.8% (200gr) and 4.2% (300gr) (by dry weight of the soil). Geosta is a secondary stabilization agent consisting of artificial zeolites A_4, chlorides and alkali. Table 1 reflects the nomenclature used for each mixture. Geosta chemical composition is shown in Table 2.

Table 1. Cement pastes nomenclature and cement and Geosta percentages.

Nomeclature	Mixed
5% OPC	
5% OPC	5% cement, 0% Geosta
5%OPC-1.4% G	5% cement, 1.4% Geosta
5%OPC-2.8% G	5% cement, 2.8% Geosta
5%OPC-4.2% G	5% cement, 4.2% Geosta
7.5% OPC	
7.5% OPC	7.5% cement, 0% Geosta
7.5% OPC-1.4% G	7.5% cement, 1.4% Geosta
7.5% OPC-2.8% G	7.5% cement, 2.8% Geosta
7.5% OPC-4.2% G	7.5% cement, 4.2% Geosta
10% OPC	
10% OPC	10% cement, 0% Geosta
10% OPC-1.4% G	10% cement, 1.4% Geosta
10% OPC-2.8% G	10% cement, 2.8% Geosta
10% OPC-4.2% G	10% cement, 4.2% Geosta

Table 2. Chemical composition of Geosta®

Component	Quantity (%)
$MgCl_2.6H_2O$ (tech. pure)	14
NaCl (tech. pure)	13
KCl (tech. pure)	11.6
$CaCl_2._2H_20$ (tech. pure)	10
Synthetic Zeolite A4	9.17
K_2CO_3 (tech. pure)	5.1
MgO (tech. pure)	5
$Na_2S_2O_3$ (Thiosulphate)	3.4
$FeCl_2$	3
$KHCO_3$	2.8
Amorphous SiO_2 (5 - 40 µm)	2.55
Na_2SO_4	2
$FeSO_4$	1.02
$Al_2(SO_4)_3$	0.31
Cobalt	0.31
Confidential component(s)	16.75

The S/S samples were subjected to the standard protocol of the Leaching Characteristics Of Moulded Or Monolithic Building And Waste Materials, "The Tank Test" (EA NEN 7375:2004) (Environmental Agency UK, 2004). The leaching experiments were performed at room temperature, (~24.8° C). The specimen tank (plastic container, with W=240mm, H=180 mm and L=290 mm) was filled with distilled water to achieve a liquid to solid ratio (L/S) of 1:5. The leachate was removed and replaced after 0.25, 1.0, 2.25, 4.0, 9.0, 16.0, 32.0 and 64.0 days (giving a total leaching time of ~128 days). Then the samples were collected and centrifuged at a speed of 10,000 rpm for 10 min. The supernatant was then analyzed, through a Flame Atomic Absorption Spectrometer (FAAS) and according to DIN 38406 (Rump, 1999).

Cube specimens of 100x100x100 mm were used for compressive strength test of the pastes. The strengths were determined at 156 days (28 days of curing time and after a leaching period of 128 days) according to ASTM 2166. The compressive strength was the average value of three samples. The test was carried out with a MTS machine of 100kN for small values and an MTS machine of 300 kN for high values. The constant rate applied on both MTS machines is 1 mm/min.

3. Results and Discussion

Table 3 lists the S/S waste acceptance criteria which are utilized to assess the effectiveness of the treatment. The leachability limits are extracted from the Interdepartmental Committee on Redevelopment of Contaminated Land (ICRCL) while the UCS limits are extracted from regulatory waste limit at a disposal site in the United Kingdom.

Table 3. Stabilized/solidified waste acceptance criteria.

Characteristic	Regulatory (acceptance)	Level (mg/kg)
28-day compressive strength (MPa)	Landfill disposal limit	0.34
Leachability (mg/kg)	Residential	130
	Allotment	230
	Commercial	1800

3.1 Leachability

The cumulative leach values of 5, 7.5 and 10% OPC-Geosta mix designs, in mg/l, are plotted against time, in days, in Fig.1 (a, b, c) respectively. The poor environmental performance of only OPC mixtures is evident when compared to the mixtures containing Geosta, however, all mixtures seem to have a downward tendency towards Ni release.

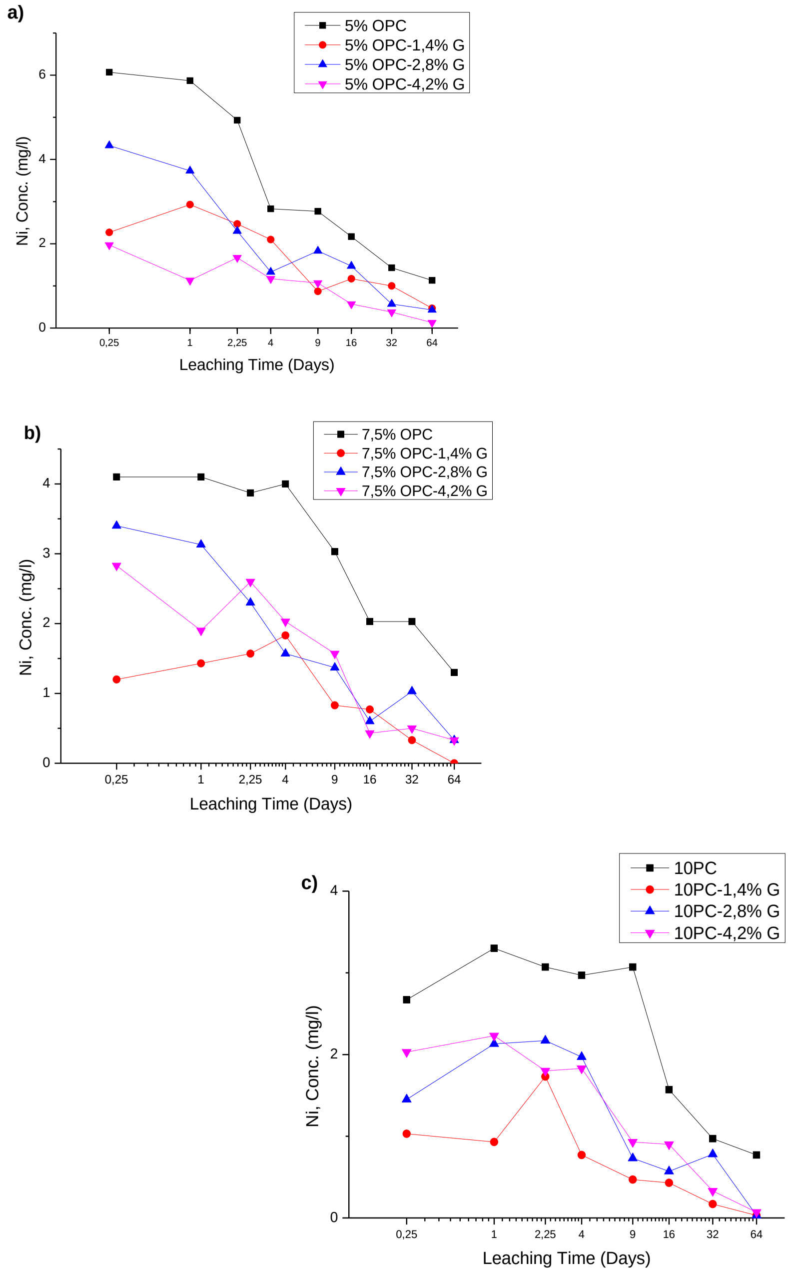

Fig. 1. Ni concentration (mg/l) and leaching time (days), for a) 5% OPC, b) 7,5% OPC, c) 10% OPC.

This poor environmental performance in the absence of Geosta relies on its chemical composition (see Table 3). Geosta is mainly composed of chlorides (MgCl, NaCl, KCl, and $CaCl_2$) and zeolites. As it has already mentioned these chlorides are good stabilizers. The key mechanism involved in producing stabilization is ion exchange between soil-cement constituents and chlorides of Geosta. More specifically, when clay particles (usually negatively charged) are covered with like-charged particles they repel each other, but if some particles have unlike charges, they attract. Then a displacement of sorbed heavy metals occurs and leads to a formation of heavy metal-Cl complexes (Dallas, 2009; Bertos, 2004; Bertos et al., 2007).

The second essential compound of Geosta is the zeolite. Zeolites are a class of alkaline porous aluminosilicates (Shi et al., 2009) with permanent negative charges on their surfaces. They have a high cation exchange capacity because their structure is made of a framework of SiO_4 and AlO_4 tetrahedra with a replacement of Si^{4+} by Al^{3+} and as a result they are natural cation exchangers and appropriate to remove toxic cations (Shi, 2009; Mahabadi et al., 2007). In fact this negative charge is balanced by exchangeable cations like calcium, potassium or sodium. On their turn these cations are exchangeable with the heavy metal cations (Li et al., 1998). As a consequence, heavy metals can be trapped inside the zeolitic structure (Terzavo et al., 2005). Due to these effects the environmental performance with the addition of Geosta is more effective and this becomes clearer in Fig. 2, where the cumulative measured leaching for Ni, for all mix designs, is presented.

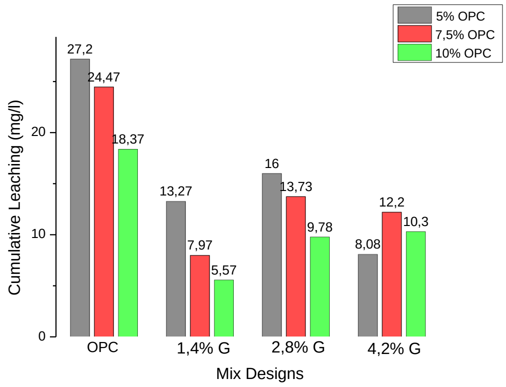

Fig. 2. Cumulative Leaching of Ni mix designs.

In mix design containing 5% OPC (see Fig 1a), the availability and release of Ni in mixtures 5%OPC-1.4%G and 5%OPC-2.8%G (containing 100 and 200g of Geosta, respectively), with 13.27 and 16.0 mg/l respectively (Fig.2), could indicate common performance patterns. However, by observing their route towards retention performance, it is obvious that 5%OPC-4.2%G mixture (containing 300g of Geosta) presents a more uniform Ni retention route, showing a weak retention ability in only one leaching phase (2.25 days) while Ni release decreases gradually throughout the duration of the test. In contrary, mixtures 5%OPC-1.4%G and 5%OPC-2.8%G present an heterogeneous Ni retention ability, with Ni release expansion observed, on the second and sixth renewal periods for 5%OPC-1.4%G and on the first (0.25 d) and fifth (9 d) renewal periods for 5%OPC-2.8%G. To conclude, S/S of Ni contaminated soil with 5% w/w cement was proved effective, for all mixtures, in retaining Ni contamination below the trigger values proposed by ICRCL. Finally, the 5%OPC-4.2%G mixture was proved more efficient in Ni confinement within its solidified matrix, since it was the only mixture that managed to maintain Ni leakage quite low 8.08mg/l.

In mix design containing 7.5% OPC (see Fig 1b), a comparison of the environmental performance of all mixtures, strengthens the earlier observation over the poor ability of cement-only mixture (7.5%OPC) to restrain Ni release. Furthermore, Geosta mixtures 7.5%OPC-1.4%G and 7.5%OPC-4.2%G, although are proved capable in Ni immobilisation when compared to 7.5%OPC, their behaviour seems to be reversed when compared to their environmental performance in the previous mix design (5% OPC). Mixture, 7.5%OPC-1.4%G shows optimum Ni restrainment in its cementitious matrix while, 7.5%OPC-2.8%G and 7.5%OPC-4.2%G exhibit similar behaviour.

In mix design containing 10% OPC (see Fig 1c), the difference in Ni release is also obvious between the OPC and the Geosta containing mixtures. Ni release for all mixtures is lower when compared to 5% OPC and 7.5%OPC mix designs, indicating that the increase in cement (10% w/w) has a critical role in Ni release from solidified material. The cumulative release of 10%OPC Mix Design (Fig.2), verifies the previous statement, since all mixtures achieve better environmental performance when compared to 5% OPC Mix design and 7.5% OPC Mix design. However, as in previous mix design (7.5% OPC), mixture 10%OPC-1.4%G demonstrates optimum Ni retention ability (5.57 mgL^{-1}) while, 10%OPC-2.8%G and 10%OPC-4.2%G performed in an antagonistic, although similar manner, by reaching cumulative concentrations of 9.78 mgL^{-1} and 10.3 mgL^{-1}, respectively.

3.2 Mechanical Properties

The long-term viability of S/S waste was further assessed by analysing the mechanical performance of the S/S material. Fig.3 (a, b, c) shows the stress-strain relation for the samples studied and Table 4 the values of Compressive Strength andElastic Modulus.

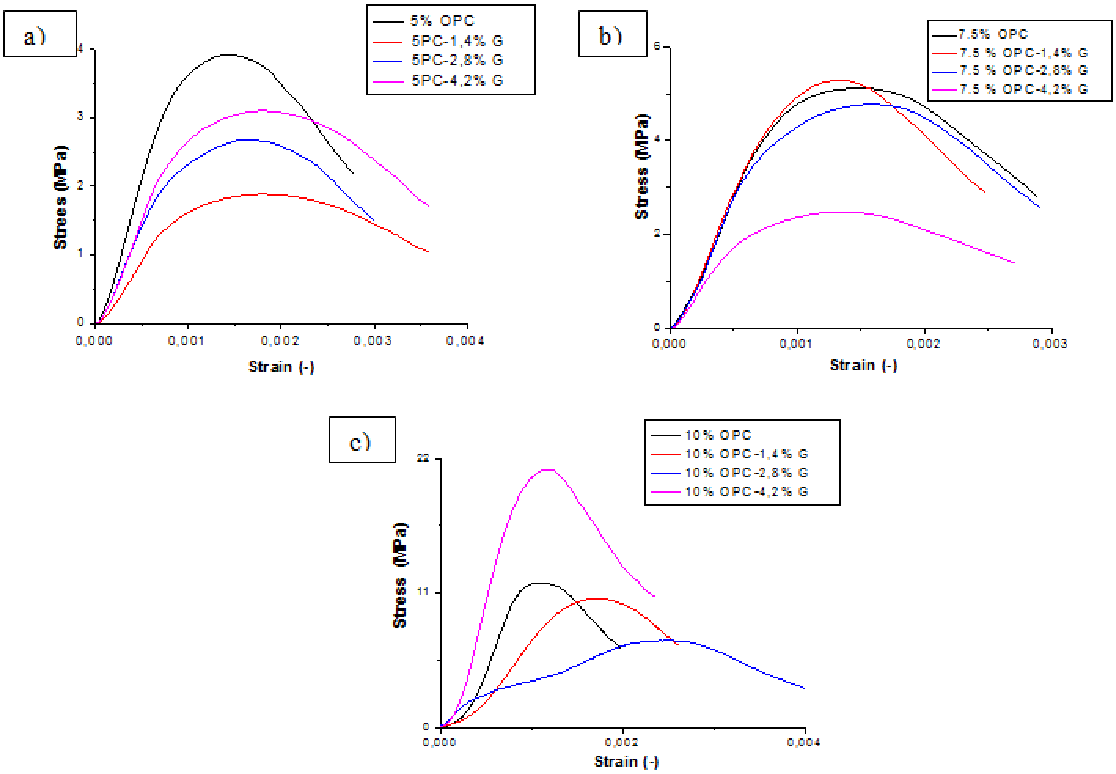

Fig. 3 Stress-strain relation of Ni contaminated soil, treated with OPCt and gesota: (a) 5% , (b) 7.5%, (c): 10%

Table 4. Elastic Modulus and Compressive Strength of mix designs.

Materials	Elastic modulus (MPa)	Compressive Strength (MPa)
5% OPC	4.2	3.9
5% OPC-1.4% G	1.75	1.9
5% OPC-2.8% G	2.75	2.7
5% OPC-4.2% G	2.84	3.1
7.5% OPC	5.46	5.1
7.5% OPC-1.4% G	5.7	5.3
7.5% OPC-2.8% G	5.28	4.8
7.5% OPC-4.2% G	3.45	2.5
10% OPC	11.8	11.84
10% OPC-1.4% G	6.5	10.51
10% OPC-2.8% G	6.2	7.11
10% OPC-4.2% G	22.75	21.11

It is evident that higher compressive strength values were obtained when higher amount of cement (OPC) was used for the solidification process. The mix design containing 10% of OPC has presented values almost three times higher than the mix design containing 7.5% OPC and four times higher when compared to the mix design containing 5% OPC. This effect could be attributed to the fact that by increasing the cement quantity, the amount of C_3S (tricalcium silicate) and C_2S (dicalcium silicate) increased in the stabilized soil enabling more production of calcium–silicate–hydrate (C-S-H) (Yin et al., 2007).

By observing Fig.3-a and Table 4 it could be conducted that 5%OPC mixture only demonstrates the highest compressive strength (3.9 MPa) with an Elastic modulus of 4,2. This result contradicts the environmental performance of the same mixture during the leaching test, as it gives the highest leaching value for 5% OPC.

Accordance with the environmental performance of S/S samples is however, observed for the mixtures in 7.5% mix design. Mixture 7.5%OPC-1.4%G demonstrates the highest increase in strength and elastic modulus, 5.3 MPa and 5,7 MPa respectively.

Nevertheless, the most striking observation was presented during the strength assessment of the final mixture 10%OPC-4.2%G (see Fig 3c). Although all samples have produced a significant increase in compressive strength when compared to the 7.5% mix design, the 10%OPC-4.2%G mixture has presented an impressive increase, reaching 21.11 MPa. This fact could be due to crystal formation since all samples appear covered with a white layer similar to that formed by the oversaturation of an inorganic salt solution (NaCl, K_2CO_3, etc) (Kontori et al., 2009).

The compressive strength values of the S/S specimens at 156 days, far exceeded the minimum landfill disposal limit of 0.34 MPa at a disposal site in the UK.

4. Conclusions

Based on the environmental and physical performance of the OPC/ Geosta-treated Ni contaminated soil, the following conclusions can be drawn:

- All mix designs managed to retain Ni contamination below the trigger values proposed by
- ICRCL.
- The introduction of Geosta into the S/S treatment increased the ability of the binder
- system over Ni retention by more than two times, when compared to only cement mixtures.
- This difference in retention ability between the plain cement mixtures and the ones
- containing Geosta could be attributed to the cation exchange ability of chlorides (formation of heavy metal-Cl complexes) and zeolites (heavy metals are trapped inside the zeolitic structure) in Geosta powder.
- In relation to the mechanical performance of S/S Ni, higher compressive strength values
- were obtained when higher amount of cement (10%OPC) was used for the solidification process.
- The optimum mixture in terms of reuse, leaching, compressive strength and cost is
- 5%OPC-4.2%G and has tremendous potential in construction material applications such as engineering fil, pavement blocks and bricks among others.

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